

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 581 274 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **93112089.3**

(51) Int. Cl.5: **D06M 23/12, D06M 13/00**

(22) Date of filing: **28.07.93**

(30) Priority: **31.07.92 JP 225359/92**
20.08.92 JP 245685/92

(43) Date of publication of application:
02.02.94 Bulletin 94/05

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI LU MC
NL PT SE

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(54) **Aroma-imparting method and aroma-emitting textile product.**

(57) Aroma-imparting method comprising the steps of: cationizing a textile product with a liquid containing a nitrogenous cationic compound; and subjecting the cationized textile product to a capsule-fixing treatment with a capsule-dispersion liquid wherein perfume-containing microcapsules are dispersed.

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The present invention relates to an aroma-imparting method for making a textile product emit an aroma, and an aroma-emitting textile product.

To make a textile product emit an aroma, there can be employed a method wherein the textile product is printed with a printing paste which contains a synthetic resin and which is supplemented with a perfume as such, and a method wherein the textile product is padded with a dispersion liquid containing a synthetic resin and a perfume as such. However, the aroma emitted by the thus-obtained textile products is rapidly lost due to volatilization, though it is initially strong. In addition, there has been trouble of staining of other textile products with the volatilized perfume during product storage (perfume transfer) and drawback of loss of almost all perfume component in a single time of washing in the consumption stage.

A perfume-containing microcapsule, wherein a perfume is contained in a microcapsule which is to be broken by an external force such as friction, emits an aroma upon capsule break; the aroma is hardly lost due to volatilization before capsule break.

Thus, if it is possible to strongly fix such perfume-containing microcapsules to a textile product and allow an appropriate amount of microcapsules to break relatively constantly over a long period of time during use of the textile product, a textile product can be obtained which emits an appropriate aroma relatively constantly over a long period of time, which is free of the problem of aroma transfer during storage and which is excellent in washing fastness.

When a textile product is padded with a dispersion liquid containing perfume-containing microcapsules and a synthetic resin, the amount of microcapsules fixed to the textile product is relatively low, but the degree of spoilage of the appearance of the obtained textile product is also relatively low. Also, when a textile product is printed with a printing paste which contains a large amount of synthetic resin and which is supplemented with perfume-containing microcapsules, in accordance with the method disclosed in Japanese Patent Examined Publication No. 47440/1978, a large amount of microcapsules can be fixed to the textile product, but the degree of spoilage of the appearance of the obtained textile product is also great. Moreover, none of these methods makes it possible to produce a textile product which emits a satisfactory aroma relatively constantly over a long period of time.

The object of the present invention is to provide an aroma-imparting method which makes it possible to strongly fix a large amount of perfume-containing microcapsules to a textile product and allow an appropriate amount of microcapsules to break and emit an appropriate aroma relatively constantly over a long period of time during use of the textile product, and an aroma-emitting textile product wherein perfume-containing microcapsules are fixed strongly and in a large amount and an appropriate amount of microcapsules break to emit an appropriate aroma relatively constantly over a long period of time during use of the textile product.

The aroma-imparting method of the present invention comprises the steps of:
cationizing a textile product with a liquid containing a nitrogenous cationic compound; and
subjecting the cationized textile product to a capsule-fixing treatment with a capsule-dispersion liquid wherein perfume-containing microcapsules are dispersed, the perfume-containing microcapsule containing at least a perfume in a microcapsule which is made essentially of a polymer compound, to fix the perfume-containing microcapsules to the textile product.

Also, the aroma-emitting textile product of the present invention is a textile product cationized by a nitrogenous cationic compound and fixed with perfume-containing microcapsules, the perfume-containing microcapsules containing at least one perfume in microcapsules made essentially of a polymer compound.

According to the aroma-imparting method of the present invention, a large amount of perfume-containing microcapsules can be strongly fixed to a textile product without spoiling the appearance and touch thereof, very few perfume-containing microcapsules drop from the textile product due to washing, and there is no problem of aroma transfer during storage of the textile product. The textile product emits an appropriate aroma as an appropriate amount of microcapsules break due to friction etc. during use relatively constantly over a long period of time.

Also, when the textile product is subjected to a binder treatment in addition, perfume-containing microcapsules fixation to the textile product is enhanced with scarcely spoiling the appearance or touch thereof and the aroma-emitting action of the textile product, almost equivalent to that without the binder treatment, is retained for a long period of time.

The aroma-emitting textile product of the present invention emits an appropriate aroma as an appropriate amount of microcapsules break due to friction etc. during use relatively constantly over a long period of time, very few perfume-containing microcapsules drop due to washing, and there is no problem of aroma transfer during storage. In addition, the appearance and touch of the original textile product is retained.

Also, in case that the aroma-emitting textile product of the present invention is treated with a binder in an amount such that the appearance or touch of the textile product is not spoiled, perfume-containing microcapsule fixation to the textile product is enhanced, and the aroma-emitting action, almost equivalent to that without the binder treatment, is retained for a long period of time.

5 Textile products

Examples of fiber used in the textile product of the present invention include cellulose fibers such as cotton and hemp, protein fibers such as wool and silk, regenerated fibers such as viscose rayon fiber, semi-
10 synthetic fibers such as acetate fiber, and synthetic fibers such as polyamide fiber, polyester fiber, acrylic fiber and polyurethane fiber.

Examples of the textile product for the present invention include yarns, slivers, loose fiber, fabrics, knittings, unwoven fabrics, and sewed products such as clothings using these fabrics, knittings or unwoven fabrics. Examples of sewed products include T-shirts, sweat shirts, jumpers, jeans, socks, bags and caps.

15 The textile product of the present invention need not consist of a single kind of fiber. For example, the yarn may be a mixed yarn of one or more kinds of fiber selected from the above-mentioned fibers, and the fabric may be an interwoven product of two or more kinds of yarn.

Also, the textile product for the present invention may have previously been colored by dyeing etc.

20 Nitrogenous cationic compounds

The nitrogenous cationic compound for the present invention is exemplified by
alkylammonium salt type compounds,
pyridinium salt type compounds,
25 dicyandiamide type compounds,
polyamine type compounds and
polycation type compounds.

Examples of nitrogenous cationic compounds are given below.

Examples of alkylammonium salt type compounds include alkylammonium salt type cationic surfactants
30 such as
trimethyloctadecylammonium chloride,
trimethylhexadecylammonium chloride,
trimethylaurylammonium chloride,
dimethylaurylammonium chloride,
35 laurylmethylammonium chloride,
lauryldimethylbenzylammonium chloride,
alkylbenzyldimethylammonium chloride,
stearylbenzyldimethylammonium chloride and
alkyltrimethylammonium chloride;
40 2,3-epoxypropyltrimethylammonium chloride;
3-chloro-2-hydroxypropyltrimethylammonium chloride; and triazine-ring-containing alkylammonium salt compounds such as those disclosed in Japanese Patent Unexamined Publication Nos. 155285/1977 and 155286/1977.

Examples of pyridinium salt type compounds include pyridinium salt type cationic surfactants such as
45 laurylpyridinium chloride and stearylamidomethylpyridinium chloride.

Examples of dicyandiamide type compounds include formalin condensation products of dicyanamide.

Examples of polyamine type compounds include condensation products of polyalkylenepolyamine and guanidine derivative,
polyethyleneimines and
50 polyamidopolyamines.

Examples of polycation type compounds include poly-4-vinylpyridine hydrochloride, polyacrylonitrile polymers and other tertiary amine polymers such as those disclosed in Japanese Patent Unexamined Publication No. 64186/1979, dimethylamine-epichlorohydrin condensation products such as those disclosed in Japanese Patent Examined Publication No. 243/1968,

55 2-methacryloxypropyltrimethylammonium salt polymers such as those disclosed in Japanese Patent Unexamined Publication No. 112480/1982,
dimethyldiallylammonium chloride polymers such as those disclosed in Japanese Patent Unexamined Publication No. 76177/1980,

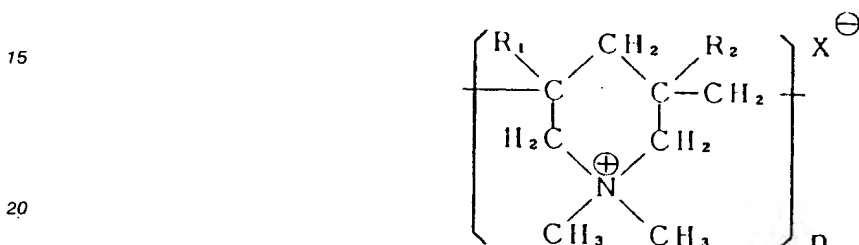
polyepichlorohydrin-trimethylamine reaction products such as those disclosed in Japanese Patent Unexamined Publication No. 112987/1976,

quaternary 1-vinylimidazole polymers, e.g. as disclosed in Japanese Patent Unexamined Publication No. 210083/1982, polymers of quaternary epoxypolyalkylenepolyamines e.g. as disclosed in Japanese Patent

Unexamined Publication Nos. 9979/1985 and 9980/1985,

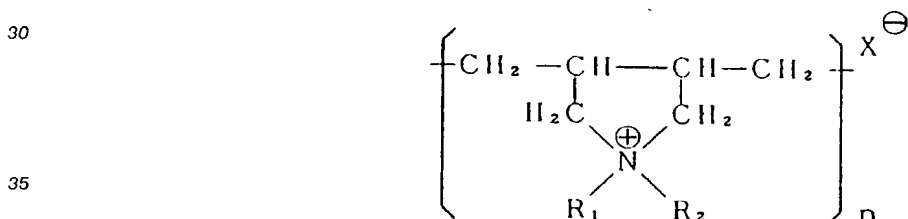
copolymers of acrylamide and cationic monomers which can copolymerize with the acrylamide, e.g. as disclosed in Japanese Patent Unexamined Publication No. 47309/1982, cationic polymers containing a quaternary ammonium base disclosed in Japanese Patent Unexamined Publication No. 234007/1988,

quaternary ammonium salt type polymers such as quaternary salts of aminoalkylacrylamide polymers disclosed in Japanese Patent Unexamined Publication No. 284225/1988, the polymer comprising the following monomer unit:



wherein X is halogen such as Cl, Br, etc., n is 50-20,000, and R₁ and R₂ is each an alkyl group having up to 20 carbon atoms,

disclosed in Japanese Patent Unexamined Publication No. 128382/1981, the polymer comprising the following monomer unit:



wherein X is halogen such as Cl, Br, etc., n is 50-20,000, and R₁ and R₂ is each an alkyl group having up to 20 carbon atoms,

(SHALLOL DC (trade name) series, product of Dai-ichi Kogyo Seiyaku Co., Ltd.), and copolymers of quaternary ammonium salts and other vinyl monomers.

Of these nitrogenous cationic compounds,

polyamine type compounds;

dicyandiamide type compounds; and

polycation type compounds such as

quaternary ammonium salt type polymers, and copolymers of quaternary ammonium salts and other vinyl monomers

are particularly effective in the present invention.

Liquids containing a nitrogenous cationic compound

Examples of liquids containing a nitrogenous cationic compound include aqueous solutions or aqueous dispersions containing a nitrogenous cationic compound and printing pastes containing a nitrogenous cationic compound.

Cationizing treatment

Cationization can be conducted for a part or all portion of the textile product, for example, in a state wherein the textile product is immersed in an aqueous solution containing a nitrogenous cationic compound.

- 5 The treatment can also be carried out by spraying such an aqueous solution on the textile product or by printing a printing paste containing a nitrogenous cationic compound on the textile product.

Perfumes

- 10 Perfumes which can be used for the present invention include water-insoluble or sparingly water-soluble natural and synthetic perfumes. These perfumes may be used in optional combinations, with auxiliaries e.g. perfume-life-extending fixatives and modifiers added as necessary. By combining one or more kinds of perfumes and auxiliaries, it is possible to obtain aromas of natural flowers such as lily of the valley, lavender, violet, rose, jasmine, carnation, lilac, hyacinth, lily, gardenia and heliotrope;
- 15 aromas of fruits such as banana, apple, pineapple, cherry and grape; musk; and other imaginary or illusionary refreshing aromas.

Examples of the above-mentioned natural perfumes include animal perfumes such as musk, civet, castreum and ambergris; vegetable perfumes such as pinene, 20 citronellol, geraniol, linalool, citral, citronellal, eugenol, safrole and menthol; and essential oils such as anise oil, kuromoji oil, abies oil, citronella oil, camphor oil, cinnamon oil, jasmine flower oil, spearmint oil, cedar oil, geranium oil, clove oil, tuberose oil, turpentine oil, neroli oil, peppermint oil, palmarosa oil, hiba oil and rosemary oil.

- Examples of the above-mentioned synthetic perfumes include terpene-based synthetic perfumes such 25 as myrcene, carvone, oxycitronellal, terpineol, hydrated terpin, 1-menthol, borneol, camphor, ionone and methylionone; and aromatic and alicyclic synthetic perfumes such as benzyl alcohol, β -phenylethyl alcohol, phenylacetaldehyde, cinnamaldehyde, α -amylcinnamaldehyde, cyclamen aldehyde, anisaldehyde, anethole, β -naphthol methyl ether, heliotropin, ethylvanillin, coumarin, isoamyl salicylate, methyl anthranilate, methyl methylanthranilate, vanillin, methylvanillin, rosephenone, alpha phenylpropyl acetate, musk ketone, 30 musk ambulet, leaf alcohol, jasmone, γ -undecalactone and Versalide (trademark).

Examples of the above-mentioned fixatives include ethyl benzoate, ethyl phthalate, benzyl salicylate, heliotropin, ethylene brassylate, iris oil and 10-oxahexadecanolide.

Examples of the above-mentioned modifiers include higher aliphatic aldehydes and isoeugenol.

35 Perfume-containing microcapsules

Containing of at least a perfume in microcapsules made essentially of a polymer compound can be achieved by, for example, the method described below.

- By carrying out a known capsulation method on a perfume described above with auxiliaries and a 40 polymer compound as coat former, and where necessary a surfactant, a protective colloid, a pH regulator, an electrolyte and other additives, perfume-containing microcapsules can be obtained in the form of, for example, an aqueous dispersion.

- Microcapsulation methods include chemical methods such as interfacial polymerization, in situ polymerization and in-liquid setting coating; physicochemical methods such as phase separation, coacervation 45 and interfacial separation; and mechanical methods such as spray drying, air suspension coating, the powder bed method and vacuum deposition.

- Also, multiple-layered microcapsules can be obtained by carrying out one or more kinds of these capsulation methods two or more times repeatedly. In any case, it is necessary to appropriately adjust microcapsule strength so that an appropriate amount of microcapsules break due to friction etc. during use 50 of the textile product to emit an appropriate aroma relatively constantly over a long period of time, according to the application, with microcapsule particle size, coat thickness and coat material in mind.

- The particle size of the perfume-containing microcapsules is preferably 0.1 to 100 μ m. Particle sizes of under 0.1 μ m result in difficulty in capsule break; in ordinary uses of the textile product, such as motion of the worn clothing, the textile product hardly emits aroma in many cases. If the particle size exceeds 100 μ 55 m, most capsules are broken by a minor external force, often resulting in perfume diffusion during production processes. More preferably, the particle size of the perfume-containing microcapsules is 1 to 50 μ m. Within this particle size range, capsules break relatively easily in ordinary use of the textile product to emit an appropriate aroma, and perfume diffusion due to capsule break during production processes is

hardly caused.

Examples of preferred coat formers include polyisocyanate and polyamine for forming a polyurea coat, polybasic acid chloride and polyamine for forming a polyamide coat, polyisocyanate and polyhydroxyl compound for forming a polyurethane coat, polybasic acid chloride and polyhydroxyl compound for forming a polyester coat, epoxy compound and polyamine for forming an epoxy resin coat, melamine-formalin prepolymer for forming a melamine coat, urea-formalin prepolymer for forming a urea resin coat, ethyl cellulose, polystyrene, polyvinylacetate, and later described anionic polymer compounds and amphoteric polymer compounds.

It is preferable that the coat for the microcapsules described above be thermosetting because of the excellent heat resistance thereof.

Examples of preferably usable surfactants and protective colloids include anionic surfactants, amphoteric surfactants, anionic polymer compounds and amphoteric polymer compounds. In addition, non-ionic surfactants can be used in combination with these.

The usual pH regulator and electrolyte used in the above capsulation methods are usable herein for the same purposes.

In the present invention, it is possible to use the perfume-containing microcapsules dispersed in a liquid dispersion which is obtained as mentioned above. From this aqueous dispersion, the surfactant and protective colloid may be removed to such an extent that it is possible to maintain the dispersion of the microcapsules. Powdery microcapsules obtained by dehydration and drying are also usable. When the powdery microcapsules are used, they are dispersed in the liquid with the surfactant and protective colloids as needed. If the microcapsules have high dispersibility, the surfactant and protective colloid are not necessary. Microcapsules, whose coat is formed of an anionic polymer compound or amphoteric polymer compound, often have enough dispersibility.

Examples of the above-mentioned anionic surfactants include alkyl sulfates, alkyl benzene sulfonates, alkyl naphthalene sulfonates, alkyl sulfosuccinates, alkyl diphenyl ether disulfonates, alkyl phosphates, polyoxyethylene alkyl sulfates, polyoxyethylene alkylaryl sulfates, polyoxyethylene alkyl ether sulfates, polyoxyethylene alkylphenyl ether sulfates, polyoxyethylene polystyrylphenyl ether sulfates, and polyoxyethylene alkyl phosphates.

Examples of the above-mentioned anionic polymer compounds include polyacrylic acid, poly- α -hydroxyacrylic acid, methacrylic acid, copolymers of these substances with other vinyl polymers, ethylene/maleic anhydride copolymer, butylene/maleic anhydride copolymer, vinyl ether/maleic anhydride copolymer, anion-modified polyvinyl alcohol, gum arabic, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, and starch derivatives.

Examples of the above-mentioned amphoteric polymer compounds include gelatin and casein.

Examples of the above-mentioned nonionic surfactants include polyoxyethylene alkyl ethers,

polyoxyethylene alkylaryl ethers, and
other polyoxyethylene derivatives;
polyoxyethylene-polyoxypropylene block copolymers,
aliphatic esters of sorbitan,

- 5 fatty acid esters of polyoxyethylene sorbitol, and
fatty acid esters of glycerol.

The perfume-containing microcapsules may be colored with a coloring agent so that the perfume-containing microcapsules impart color simultaneously with aroma to the textile product. The coloring of the perfume-containing microcapsules can be achieved by, for example, adding a coloring agent to the coat
10 former in production process of the perfume-containing microcapsules.

Examples of the coloring agent include various organic pigments such as insoluble azo pigments, phthalocyanine pigments, vat dye pigments, basic dye lakes and acid dye lakes; inorganic pigments such as titanium white, chromium yellow, cadmium red, iron oxide, carbon black and ultramarine; direct dyes; acid dyes; reactive dyes; and basic dyes. It is also possible to use, for example, fluorescent pigments, oil-
15 soluble dyes, disperse dyes, solid-solution type daylight fluorescent pigments.

Capsule-dispersion liquids

Capsule dispersion liquids include aqueous dispersions containing perfume-containing microcapsules
20 dispersed therein and printing pastes containing perfume-containing microcapsules dispersed therein.

Capsule-fixing treatment

Capsule-fixing treatment can be conducted for a part or all portion of the textile product, for example, in
25 a manner wherein the textile product is immersed in an aqueous dispersion containing perfume-containing microcapsules dispersed therein. The treatment can also be achieved by spraying such an aqueous dispersion on the textile product or by printing a printing paste containing perfume-containing microcapsules dispersed therein on the textile product.

30 Examples of aroma-imparting process

A textile product can be imparted with an aroma by the aroma-imparting method of the present invention for example as follows:

The textile product described above is first scoured, i.e. scrubbed vigorously, to remove thickening
35 agent and impurities. Scouring is of course unnecessary when the textile product is clean.

Next, to an appropriate immersion bath vat, water is added in a weight amount 5 to 50 times the weight amount of the textile product (bath ratio 5:1 to 50:1), preferably 10 to 30 times (bath ratio 10:1 to 30:1), followed by addition of a nitrogenous cationic compound in a ratio of 0.1 to 20% by weight, preferably about 0.3 to 5% by weight, relative to the untreated textile product. An acid such as acetic, tartaric, oxalic or
40 malic acid may be added to adjust the pH to the acidic side, or an alkali such as caustic soda or sodium carbonate may be added to adjust the pH to the alkaline side. A wetting agent such as urea, glycerol, ethylene glycol, polyethylene glycol and diethylene glycol may also be added as necessary to improve the permeability of the cationic compound into the textile product.

Next, the textile product described above is immersed in the aqueous solution thus obtained (an
45 example liquid containing a nitrogenous cationic compound), and the temperature is maintained at normal to about 80 °C for about 5 to 30 minutes, whereby the textile product is efficiently cationized, i.e. it is cationically modified to render its surface receptive to adsorption and adherence of the perfume-containing microcapsules.

Subsequently, this textile product is thoroughly rinsed to wash down the excess portion of the
50 nitrogenous cationic compound and other additives, and then dewatered, i.e. squeezed to damp condition.

Next, to the meanwhile emptied vat containing the thus-treated textile product, water is added in a weight ratio of about 5:1 to 50:1, preferably 10:1 to 30:1, relative to the untreated textile product, and the perfume-containing microcapsules as described above are added and dispersed in a ratio of 0.1 to 50% by weight, preferably 1 to 25% by weight, relative to the untreated textile product. The perfume-containing
55 microcapsules may be added in the form of a dispersion liquid containing them.

The cationized textile product is treated in the dispersion liquid thus obtained (an example capsule-dispersion liquid) at normal temperature to about 90 °C for about 5 to 30 minutes, whereby the perfume-containing microcapsules are almost completely exhausted into the cationized textile product, in that the

dispersed microcapsules are taken up by the textile product so that essentially no perfume-containing microcapsules are left in the liquid remaining in the vat. This treating temperature is preferably about 60 to 90 °C when using the perfume-containing microcapsules described above at high concentrations of 10 to 50% by weight.

5 This treatment results in the binding of the perfume-containing microcapsules described above to the textile product described above by chemical ionic bonding and physical adsorption. This product is then dewatered (squeezed damp) and dried, whereby the perfume-containing microcapsules are firmly and in a large amount fixed to the textile product. For enhancing this fixation, it is preferable that the textile product is subjected to heat treatment at about 80 to 180 °C for about 0.5 to 10 minutes after drying.

10 The textile product thus obtained has a large amount of perfume-containing microcapsules fixed thereto, retains the soft touch of the original textile product, and has good appearance and excellent washing fastness.

Preferable embodiments of aroma imparting

15 A preferable embodiment of the aroma-imparting method of the present invention comprises the step of treating a textile product with a binder in an amount insufficient to spoil the appearance and touch of the textile product.

The textile product obtained via this binder treatment step has improved washing fastness as a result of enhanced fixation of perfume-containing microcapsules to the textile product.

The amount of binder, as of the binder solid content, is about 0.1 to 10% by weight in general, preferably 0.3 to 5% by weight, relative to the textile product.

Examples of the usable binders include

acrylic acid ester resin,

25 methacrylic acid ester resin, vinyl acetate resin,

polyurethane resin,

polyester resin,

styrene-butadiene latex,

polyolefin resin; and

30 of the above-mentioned anionic polymer compounds,

polyacrylic acid,

methacrylic acid, and

derivatives thereof; and

copolymers of these substances with other vinyl monomers. For the present invention, acrylic acid ester

35 resin and polyurethane resin are especially preferable.

The binder treatment can be carried out by, for example, immersing the textile product in a binder-containing aqueous liquid:

spraying a binder-containing aqueous liquid on the textile product; or

40 printing a binder-containing printing paste on the textile product.

An aroma can be imparted to the textile product by this embodiment as follows for example:

Aroma-imparting Process 1

45 After a textile product is treated (cationized) with an aqueous solution containing a nitrogenous cationic compound, it is immersed for a treatment (fixing-treatment) in a dispersion containing the above-described perfume-containing microcapsules so that the perfume-containing microcapsules are exhausted into the textile product. To this liquid, a binder is added in a ratio of 0.1 to 10% by weight, as of the binder solid content, relative to the textile product, followed by a treatment (binder treatment) at a normal temperature to

50 90 °C for 1 to 30 minutes, after which the textile product is dewatered and dried.

Aroma-imparting Process 2

55 After a textile product is treated (cationized) with an aqueous solution containing a nitrogenous cationic compound, it is immersed for a treatment (fixing-treatment) in a dispersion containing the above-described perfume-containing microcapsules so that the perfume-containing microcapsules are exhausted into the textile product, followed by dewatering. Then to a container containing the textile product, water is added in a bath ratio of about 5:1 to 50:1, preferably 10:1 to 30:1, and a binder is added in a ratio of 0.1 to 10% by

weight, as of the binder solid content, relative to the textile product, followed by a treatment (binder treatment) at a normal temperature to 90 °C for 5 to 30 minutes, after which the textile product is dewatered and dried.

5 Aroma-imparting Process 3

After a textile product is treated (cationized) with an aqueous solution containing a nitrogenous cationic compound, it is immersed in a dispersion containing the above-described perfume-containing microcapsules and a binder in a ratio of 0.1 to 10% by weight, as of the binder solid content, relative to the textile product and treated (fixing-treatment and binder treatment) at a normal temperature to 90 °C for 5 to 30 minutes, after which the textile product is dewatered and dried.

Aroma-imparting Process 4

After a textile product is treated with an aqueous solution containing a nitrogenous cationic compound and a binder in a ratio of 0.1 to 10% by weight, as of the binder solid content, relative to the textile product (first step, cationization and binder treatment), it is immersed for a treatment at a normal temperature to 90 °C for 1 to 30 minutes (second step, fixing-treatment) in a dispersion containing the above-described perfume-containing microcapsules so that the perfume-containing microcapsules are exhausted into the textile product. After this treatment, the textile product is dewatered and dried.

In the first step, neutralization of the cationic compound by adding soda ash, caustic soda, etc is carried out as needed.

Also, in the first step, the combination of nitrogenous cationic compound and binder can be replaced by a cationic binder which is nitrogenous cationic compound, in an amount such that the appearance and touch of the textile product is not spoiled.

Examples of such cationic binders include

Voncoat SFC Series (trade name, emulsion of vinyl acetates or acrylic esters, product of Dainippon Ink & Chemicals, Inc.),

Yodosol AF Series (trade name, emulsion of acrylic esters, product of Kanebo N.S.C. Limited),

the CGC Series (trade name, emulsion of acrylic esters, product of Sumitomo Chemical Co., Ltd.),

cationic emulsions disclosed in Japanese Patent Unexamined Publication No. 187702/1987,

cationic copolymer disclosed in Japanese Patent Unexamined Publication No. 131003/1987,

cationic polymer disclosed in Japanese Patent Unexamined Publication No. 201914/1987, and

cationic latex disclosed in Japanese Patent Unexamined Publication No. 263211/1987.

In the above described preferable aroma-imparting processes 1 through 4, the binder is exhausted, i.e. taken up, into the textile product in an amount approximately equal to the content of the binder-containing liquid, i. e. in a ratio of about 0.1 to 10% by weight of binder solid content relative to the textile product, and the binder is strongly fixed to the textile product by dewatering and drying. As a result, further improvements in the fastness to rubbing and washing are obtained. If the binder solid content is less than 0.1% by weight, the obtained effect is likely to be insufficient. If the binder solid content exceeds 10% by weight, the appearance and touch of the textile product are often spoiled.

In the aroma-imparting method of the present invention described above, a coloring agent including the coloring agents exemplified for coloring the perfume-containing microcapsule, another coloring agent such as a thermochromic material or a photochromic material, may be incorporated in the capsule-dispersion liquid wherein perfume-containing microcapsules are dispersed, so that these coloring agents are exhausted into the textile product simultaneously with the exhaustion of the perfume-incorporating microcapsules. This makes it possible to realize constant coloring and reversible color changes depending on temperature change or on presence or absence of light irradiation, simultaneously with aroma imparting.

Examples of thermochromic materials include materials disclosed in EP-A-0480162, such as three-component mixtures of an acid developing substance, an acidic substance and a solvent; two-component mixtures of an acid developing substance and an acidic substance; cholesteric liquid crystals; and metal complex salts.

Examples of photochromic materials include organic photochromic materials such as

azobenzene compounds,
thioindigo compounds,
dithizone metal complexes,
spiropyran compounds,

spirooxazine compounds,
fulgide compounds,
dihydroprene compounds,
spirothiopyran compounds,

5 1,4-2H-oxazine,
triphenylmethane compounds,
viologen compounds, and
naphthopyran compounds.

Specifically, materials disclosed in the same publication EP-A-0480162 may be mentioned. In the present
10 invention, spiropyran compounds, spirooxazine compounds, fulgide compounds and naphthopyran com-
pounds are particularly preferable.

Also, the textile product, previously colored, may be subjected to the aroma-imparting method of the
present invention described above.

15 PREPARATION EXAMPLES OF PERFUME-CONTAINING MICROCAPSULES

Some preparation examples of perfume-containing microcapsules are given below. In the description
below, "part(s) by weight" is referred to as "part(s)".

20 Preparation Example 1

To 30 parts of an aqueous solution of 10% (w/w) gelatin being kept at 40 °C , 12 parts of WOODY 4319
(trade name for synthetic perfume, product of Kotobuki Perfumery Co., Ltd.) was added, followed by
emulsification at a stirring speed adjusted to have a particle size of about 10 μ m. Subsequently, 30 parts of
25 an aqueous solution of 10% (w/w) gum arabic being kept at 40 °C was added to this mixture, followed by
stirring for 10 minutes. To this mixture, 128 parts of 40 °C water was added. After acetic acid was added
drop by drop to reduce the pH below 4 to 4.3, the mixture was cooled to 5 °C , and 1 part of 30% (w/w)
formalin and several drops of an aqueous solution of 10% (w/w) caustic soda were added to obtain a pH of
9. Then the temperature was increased to 50 °C at a rate of 1 °C per minute. After this temperature was
30 maintained for 1 hour, the mixture was left to cool to yield about 200 parts of dispersion liquid wherein
perfume-containing microcapsules were dispersed.

Preparation Example 2

35 To 300 parts of an aqueous solution of 3% (w/w) EMA31 (trade name for ethylene-maleic acid
copolymer, product of Monsanto Company) being kept at 60 °C , 20 parts of LEMON 4314 (trade name for
a synthetic perfume, product of Kotobuki Perfumery Co., Ltd.) and 60 parts of cetyl alcohol, previously
heated and mixed at 60 °C , were added, followed by emulsification at a stirring speed adjusted to have a
particle size of about 5 μ m. To this emulsion was added drop by drop a melamine prepolymer prepared
40 by reacting 30 parts of 37% (w/w) formalin and 10 parts of melamine at 60 °C for 10 minutes. After
completion of the dropwise addition, the liquid temperature was increased to 80 °C , followed by heating
and stirring for 30 minutes, to yield 420 parts of dispersion liquid wherein perfume-containing microcapsules
were dispersed.

45 Preparation Example 3

To 300 parts of an aqueous solution containing 3 parts of DEMOL N (trade name for an anionic
surfactant, product of Kao Corporation), mixture of 30 parts of ROSE 4316 (trade name for synthetic
perfume, product of Kotobuki Perfumery Co., Ltd.) 40 parts of DINP (plasticizer) and 30 parts of SUMIDUR
50 N75 (trade name for aliphatic polyisocyanate, product of Sumitomo Bayer Urethane Co., Ltd.), kept at 80
°C was added drop by drop, followed by emulsification at a stirring speed adjusted to have a particle size
of about 2 μ m. About 15 minutes later, the liquid temperature was increased to 95 °C , followed by heating
and stirring for 2 hours, to yield about 400 parts of dispersion liquid wherein perfume-containing micro-
capsules were dispersed.

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Preparation Example 4

To 196 parts of an aqueous solution of 2% polyvinyl alcohol, mixture of 35 parts of PEPPERMINT 4234 (trade name for synthetic perfume, product of Kotobuki Perfumery Co., Ltd.), 55 parts of CRYSTOL 352 (trade name for liquid paraffin, product of Esso Sekiyu K.K.), 20 parts of EPIKOTE 828 (trade name for epoxy resin, product of Yuka Shell Epoxy Co.) and 2 parts of FLEX BLUE BASE (trade name for phthalocyanine, product of Matsui Shikiso Chemical Co., Ltd.), kept at 80 °C, were added drop by drop, followed by emulsification at a stirring speed adjusted to have a particle size of about 15 μ m. Next, 12 parts of EPICURE U (trade name for hardener, product of Yuka Shell Epoxy Co.) was added drop by drop, followed by a reaction for 2 hours with heating and stirring, to yield about 320 parts of dispersion liquid wherein blue-colored perfume-containing microcapsules were dispersed.

EXAMPLES

Some examples are given below to illustrate, without limitation, the present invention.

Example 1

First, a cotton T-shirt (sheeting, 120 parts) was scoured, i.e. scrubbed vigorously, to remove the thickening agents and impurities.

Next, to a 5-liter vat were added 2400 parts of water (bath ratio 20:1), 2 parts of SANFIX PAC-7 (trade name for aqueous solution of nitrogenous cationic polymer compound, product of Sanyo Chemical Industries, Ltd.) and 10 parts of ethylene glycol.

The scoured T-shirt was immersed in this aqueous solution followed by gradual temperature rise and treatment at 70 °C for 15 minutes.

The T-shirt was thoroughly rinsed with water to remove the excess portion of the nitrogenous cationic polymer compound and other additives and then dewatered, i.e. squeezed to damp condition.

Next, to a 5-liter vat, the dewatered T-shirt, 2400 parts of water, 10 parts of the perfume-containing microcapsule dispersion liquid obtained in Preparation Example 1 and 25 parts of CHROMICOLOR AQUALITE INK FAST BLUE AQ-27 (trade name for thermochromic color, product of Matsui Shikiso Chemical Co., Ltd.) were added. The liquid temperature was gradually increased, followed by treatment at 80 °C for 15 minutes. The perfume-containing microcapsules were completely taken up by the T-shirt.

Subsequently, this T-shirt was thoroughly rinsed and dewatered, after which it was allowed to dry and then subjected to heat treatment at 140 °C in a tumbler drier for 1 minute.

The T-shirt thus obtained was found to retain the original appearance and touch. When a person wearing this T-shirt jogged lightly, wood aroma was emitted and the jogger felt refreshing as if running in woods. Also, with the rise in body temperature, the T-shirt changed its color from blue to white.

This aroma-emitting and reversibly color changing function was not lost even after repeated washing.

Example 2

Process from a cotton T-shirt's (sheeting 120 parts) taking up of CHROMICOLOR AQUALITE INK FAST BLUE AQ-27 and perfume-containing microcapsules to water rinsing and dewatering of the T-shirt was carried out in the same manner as in Example 1.

Next, to a vat containing the T-shirt, 2400 parts of water and 12 parts (solid content about 3.6 parts) of MATSUMINZOL MR-10 (trade name for emulsion of acrylic ester resin, product of Matsui Shikiso Chemical Co., Ltd.) were added, followed by gradual temperature rise and treatment at 70 °C for 15 minutes, after which the T-shirt was dewatered and dried.

The T-shirt thus obtained showed the same function with that in Example 1, and had good appearance and touch, comparable to those in Example 1, and further improved washing fastness.

Example 3

A cotton T-shirt was treated in the same manner as in Example 1 except that CHROMICOLOR AQUALITE INK FAST BLUE AQ-27 was replaced by 25 parts of PHOTOPIA AQUALITE INK PURPLE AQ-R (trade name for photochromic color, product of Matsui Shikiso Chemical Co., Ltd.).

The T-shirt thus obtained emitted wood aroma as the wearer made gentle motions, and the wearer felt refreshing as if staying in woods. Also, when the wearer went outdoors, the portions exposed to sunlight

became deep purple. The appearance, touch, washing fastness and other quality factors were as good as those in Example 1.

Example 4

First, a cotton sweat shirt (300 parts) was scoured to remove thickening agent and impurities.

Next, to a 10-liter vat, 6000 parts of water, 2.7 parts of SANFIX 70 (trade name for a nitrogenous cationic polymer compound, product of Sanyo Chemical Industries, Ltd.) and 15 parts of ethylene glycol were added. The sweat shirt was immersed in this liquid, followed by treatment at 60 °C for 15 minutes, after which the sweat shirt was thoroughly rinsed and then dewatered.

Next, to a 10-liter vat containing this sweat shirt, 6000 parts of water were added, and 45 parts of the perfume-containing microcapsule dispersion liquid obtained in Preparation Example 2 was added therein and dispersed. The liquid temperature was gradually increased, followed by treatment for 15 minutes, after which the cotton sweat shirt was thoroughly rinsed and then dewatered.

Next, to a 10-liter container containing this sweat shirt, 6000 parts of water were added, and 30 parts of HYDRAN AP-20 (trade name for polyurethane resin emulsion, product of Dainippon Ink & Chemicals, Inc.) was added. After the liquid temperature was gradually increased, followed by treatment at 70 °C for 15 minutes, the cotton sweat shirt was dewatered and allowed to dry well.

When the wearer of this sweat shirt made light exercise, the microcapsules were broken by friction, and lemon aroma was emitted. The touch, appearance and washing fastness of the sweat shirt were all good.

Example 5

An acrylic shirt (120 parts) was scoured to remove thickening agent and impurities.

Next, to a 5-liter container, 2400 parts of water (bath ratio 20:1), 4 parts of SANFIX PAC-7 (trade name for aqueous solution of nitrogenous cationic polymer compound, product of Sanyo Chemical Industries, Ltd.) and 6 parts of MATSUMINZOL MR-C (trade name for emulsion of acrylic ester resin, product of Matsui Shikiso Chemical Co., Ltd.) were added. In this mixture the scoured shirt was immersed, followed by gradual temperature rise and treatment at 70 °C for 15 minutes.

Subsequently, the shirt was thoroughly rinsed and then dewatered.

Next, to a 5-liter container, 2400 parts of water and 10 parts of the perfume-containing microcapsules obtained in Preparation Example 4 were added, and the dewatered shirt was immersed therein.

The liquid temperature was gradually increased, followed by treatment at 70 °C for 15 minutes. This treating solution changed from blue to colorless transparent, demonstrating complete exhaustion.

Next, this shirt was thoroughly rinsed and dewatered, after which it was dried well.

The shirt thus obtained was found to retain the original touch and appearance and have a blue color. As the wearer of this shirt made gentle motions, a refreshing peppermint aroma became perceptible. This function was not lost even after repeated washing.

Example 6

To a 5-liter vat, 2400 parts of water (bath ratio 20:1), 2 parts of SANFIX PAC-7 (trade name for aqueous solution of nitrogenous cationic polymer compound, product of Sanyo Chemical Industries, Ltd.) and 10 parts of ethylene glycol were added.

In this aqueous solution was immersed a polyester/cotton mixed yarn blouse (120 parts) previously printed with rose flower patterns with an ordinary printing ink by means of a screen, followed by gradual temperature rise and treatment at 70 °C for 15 minutes.

Subsequently, the blouse was rinsed with water to remove the excess portion of nitrogenous cationic compound and other additives and then dewatered.

Next, to a 5-liter vat containing the dewatered blouse 2400 parts of water and 20 parts of the perfume-containing microcapsule dispersion liquid obtained in Preparation Example 3 were added, followed by gradual temperature rise and treatment at 80 °C for 15 minutes.

The blouse thus obtained was found to retain the original touch and appearance. As the wearer made gentle motions or upon friction with a sofa, for instance, the microcapsules were broken and a fragrant rose aroma became perceptible.

This function was not lost even after repeated washing.

Comparative Example 1

A T-shirt was treated in exactly the same manner as in Example 1 except that the perfume-containing microcapsule dispersion liquid obtained in Preparation Example 1 was replaced by 10 parts of an emulsion of 12 parts of Woody 4319 in 188 parts of surfactant-containing water. This T-shirt was of no commercial value; the perfume was almost completely lost during the drying process, and the trace residual aroma was totally lost in one time of washing.

Comparative Example 2

A T-shirt treated in exactly the same manner as in Example 1 except that no nitrogenous cationic compound was used was of no commercial value; the aroma was weak and no aroma was emitted after several times of friction because the perfume-containing microcapsules were not completely exhausted into the T-shirt.

Comparative Example 3

The same T-shirt as used in Example 1 was scoured to remove thickening agents and impurities.

Next, to a 5-liter vat, 2400 parts of water, 100 parts of the perfume-containing microcapsule dispersion liquid obtained in Preparation Example 1 and 120 parts of MATSUMINZOL MR-10 were added. Using this mixture liquid, the above-mentioned T-shirt, not cationized, was treated by the two-dip two-rinse method.

In this treatment, the perfume-containing microcapsules were hardly exhausted into the T-shirt. The obtained T-shirt was of no commercial value because it was poor in aroma emission and had a rough touch.

Next, the products obtained in Example 1 and Comparative Examples 1, 2 and 3 were compared with respect to aroma strength, aroma-emitting function retainability, appearance and touch, and washing fastness. The results are given in Table 1.

In Table 1, O indicates a good result, and X indicates a poor result.

TABLE 1

	aroma strength	aroma-emitting function retainability	appearance and touch	washing fastness
Example 1	O	O	O	O
Comparative Example 1	X	X	O	X
Comparative Example 2	X	X	O	X
Comparative Example 3	X	X	X	X

Claims

1. Aroma-imparting method comprising the steps of: cationizing a textile product with a liquid containing a nitrogenous cationic compound; and
subjecting the cationized textile product to a capsule-fixing treatment with a capsule-dispersion liquid wherein perfume-containing microcapsules are dispersed, the perfume-containing microcapsule containing at least a perfume in a microcapsule which is made essentially of a polymer compound, to fix the perfume-containing microcapsules to the textile product.
2. Aroma-imparting method of claim 1 wherein the nitrogenous cationic compound is a member of the group consisting of alkylammonium salts, pyridinium salts, dicyandiamides, polyamines and polycations.
3. Aroma-imparting method of claim 2 wherein the polycation is a member of the group consisting of poly-4-vinylpyridine hydrochloride, tertiary amine polymers, polymers of quaternary ammonium salts and copolymers of quaternary ammonium salts and vinyl monomers.

4. Aroma-imparting method of claim 1, 2 or 3 wherein the perfume-containing microcapsules are included in the capsule-dispersion liquid in a ratio of about 0.1 to 50% by weight relative to the textile product.
- 5 5. Aroma-imparting method of claim 1, 2, 3 or 4 including treating the textile product with a binder for physically binding the perfume-containing microcapsules to the textile product.
6. Aroma-imparting method of claim 5 wherein the binder is a solid containing binder and is used in an amount of about 0.1 to 10 % by weight binder solid content relative to the textile product.
- 10 7. Aroma-imparting method of claim 1, 2, 3, 4, 5 or 6 wherein the capsule-fixing treatment is conducted by immersing the textile product in the capsule-dispersion liquid.
8. Aroma-imparting method of claim 1, 2, 3, 4, 5 or 6 wherein the capsule-dispersion liquid is in the form of a printing paste, and the capsule-fixing treatment is conducted by printing the paste on the textile
15 product.
9. Aroma-imparting method of claim 5 or 6 wherein the capsule-fixing treatment is conducted by immersing the textile product in the capsule-dispersion liquid, after which the binder is added to the residual liquid and the textile product is treated with binder.
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10. Aroma-imparting method of claim 5 or 6 wherein cationization of the textile product is conducted substantially simultaneously with treating the textile product with a binder.
11. Aroma-imparting method of claim 10 wherein the nitrogenous cationic compound contained in the liquid
25 is a cationic binder.
12. Aroma-imparting method of claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11 wherein the liquid containing a nitrogenous cationic compound is in the form of a printing paste, and the cationizing treatment is conducted by printing the paste on the textile product.
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13. Aroma-imparting method of claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12 wherein the textile product has previously been colored.
14. Aroma-imparting method of claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 or 13 wherein the perfume-
35 containing microcapsules have previously been colored with a coloring agent.
15. Aroma-imparting method of claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 or 14 wherein the capsule-dispersion liquid contains a coloring agent.
- 40 16. Aroma-imparting method of claim 15 wherein at least a part of the coloring agent is thermochromic or photochromic.
17. Aroma-emitting textile product cationized by a nitrogenous cationic compound and fixed with perfume-containing microcapsules, the perfume-containing microcapsule containing at least a perfume in a microcapsule which is made essentially of a polymer compound.
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18. Aroma-emitting textile product of claim 17 wherein the perfume-containing microcapsules are physically bound to the textile product by a binder.
- 50 19. Aroma-emitting textile product of claim 17 or 18 wherein the textile product is colored with a coloring agent.
20. Aroma-emitting textile product of claim 19 wherein at least a part of the coloring agent is thermochromic or photochromic.
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21. Aroma-emitting textile product of claim 17, 18, 19 or 20 wherein the perfume-containing microcapsules are colored by a coloring agent.



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EUROPEAN SEARCH REPORT

Application Number
EP 93 11 2089

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	EP-A-0 480 162 (MATSUI SHIKISO CHEMICAL CO., LTD.) * page 3, line 20 - page 4, line 28 * * page 5, line 55 - page 6, line 43 * * page 7, line 15 - line 46; claims; examples * ---	1-21	D06M23/12 D06M13/00
A	US-A-4 234 627 (SCHILLING) * column 5, line 5 - line 49; claims * ---	1	
A	US-A-4 326 967 (MELVILLE) * the whole document * ---	1	
A	EP-A-0 328 937 (KANEBO LTD.) * the whole document * ---	1	
A	PATENT ABSTRACTS OF JAPAN vol. 015, no. 421 (C-0878)25 October 1991 & JP-A-03 174 073 (KOGYO KK) 29 July 1991 * abstract * ---	1	
A	PATENT ABSTRACTS OF JAPAN vol. 015, no. 456 (C-0886)20 November 1991 & JP-A-03 193 979 (UNITIKA LTD.) 23 August 1991 * abstract * & DATABASE WPI Week 9140, Derwent Publications Ltd., London, GB; AN 91-291888 & JP-A-3 193 979 (UNITIKA) 23 August 1991 * abstract * -----	1	TECHNICAL FIELDS SEARCHED (Int.Cl.5) D06M D06Q D06P
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 5 November 1993	Examiner BLAS, V
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			

